



(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 317 273
A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 88310786.4

(51) Int. Cl.⁴: C08L 75/04 , D01F 6/70 ,
D01F 1/02

(22) Date of filing: 15.11.88

(30) Priority: 16.11.87 US 121272

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(43) Date of publication of application:
24.05.89 Bulletin 89/21

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DE FR GB IT NL

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(54) Improved spinning of spandex filaments.

(57) An improved process is provided for dry spinning spandex filaments which contain titanium dioxide pigment particles and a polymeric tertiary amine stabilizer. An organic base, such as ethylene diamine or diethyl amine, is added to the polymer solution before the titanium dioxide or the polymeric amine stabilizer is added to the solution. Improved spinning continuity and product yield are obtained.

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Improved Spinning of Spandex Filaments**BACKGROUND OF THE INVENTION**

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Field of the Invention

This invention relates to a process for preparing spandex filaments in which a solution of the polymer contains a tertiary amine stabilizer and titanium dioxide particles. In particular, the invention concerns 10 improvements in such a process wherein the addition of an organic base to the solution results in improved processing and product yields.

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Description of the Prior Art

Spandex filaments are well known and have found considerable utility and commercial success in a large variety of fabrics. Many processes have been disclosed for the manufacture of spandex filaments from solutions of spandex polymer. Dry spinning is used extensively.

The need for special stabilizers and other agents in spandex filaments has led to inclusion of various 20 organic and inorganic compounds in the filaments. Additives, such as fillers, pigments, plasticizers and stabilizers against degradation by oxygen, chlorine, heat, fumes or ultra-violet light, are often incorporated into the filaments by being added to the polymer solution prior to spinning. In the polymer solution, the additives may dissolve or form a slurry.

Hunt, United States Patent 3,428,711, the entire disclosure of which is hereby incorporated by 25 reference, describes polymeric tertiary-aminoalkyl acrylates and methacrylates, which are partially suited for use as stabilizers and/or dye enhancers for spandex fibers. Such stabilizers (and/or dye enhancers) have been used in commercial spandex yarns for many years. Pigments, such as particles of titanium dioxide, also have long been used as whiteners for such fibers. However, the present inventor noted that dry spinning of spandex fibers from polymer solutions in which either the Hunt stabilizer or the TiO₂ was 30 included alone resulted in easier processing and higher yields of satisfactory product than when both the stabilizer and the TiO₂ were included together. Accordingly, an object of this invention is to provide an improved process for dry-spinning spandex fibers that contain as additives, both, TiO₂ particles and a polymeric tertiary amine stabilizer.

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SUMMARY OF THE INVENTION

The present invention provides an improved process for dry-spinning spandex filaments, wherein a 40 polymeric, hindered tertiary amine stabilizer and acidic inorganic particles are added to a spandex polymer solution prior to spinning. The improvement of the present invention comprises adding to the polymer solution an effective amount of a soluble organic base, either before the amine stabilizer is added or before the inorganic particles are added to the polymer solution. Preferably, the inorganic particles are titanium dioxide particles and the base is an amine that provides the polymer solution with 0.04 to 1.0 gram 45 equivalents of amine units per kilogram of titanium dioxide. Most preferably the amine is diethyl amine or ethylene diamine. In a further preferred embodiment, the titanium dioxide has a concentration in the range of 1 to 7 percent and the polymeric stabilizer is a sterically hindered, tertiary-aminoalkyl acrylate and/or methacrylate polymer, having a concentration in the range of 0.5 to 10 percent, both percentages being based on the weight of the polymer in solution. As a result of the addition of the base, dry-spinning 50 continuity and yield of spandex filaments are improved significantly.

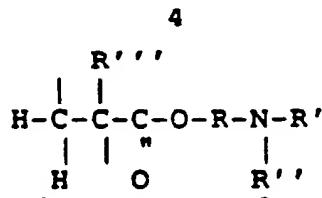
DESCRIPTION OF PREFERRED EMBODIMENTS

As used herein, the term "spandex" means a fiber-forming, long chain, synthetic organic polymer comprised of at least 85% of segmented polyurethane. Preferred spandex polymers for use in the present invention are those having polyether or polyester soft segments. Such polymers are well known in the art and are made by processes, such as those referred to in United States Patent 3,428,711, Column 2, lines 5 26-29. The present invention is found to be most useful in improving the spinning of polyether-based spandex solutions.

Bases suitable for use in the present invention are soluble organic compounds, preferably amines, usually having having a pK_b in the range of about 2.5 to 5, preferably in the range of 3 to 4.2. Among suitable amine bases are ethylene diamine, diethyl amine, n-butyl amine, n-propyl amine and the like, the 10 first two mentioned amines being the most preferred.

The concentration of soluble organic base that is effective in improving the spinnability of the spandex polymer solution and the yield of good-quality filaments, in accordance with the present invention, can vary over a wide range. When organic amines are used in accordance with the invention, some beneficial effects 15 usually are noted when the organic amine provides as little as 0.04 gram equivalent of amine units to the polymer solution per kilogram of TiO_2 that is present or that will be present in the polymer solution. Provision of more than 1.0 gram equivalent of amine units per kilogram of TiO_2 usually is not necessary. The most preferred concentration range of amine units is 0.1 to 0.5 gram equivalent per kilogram of TiO_2 .

The polymeric amine stabilizers that are present in the polymer solutions according to the process of the present invention are usually polymeric tertiary amines, preferably sterically hindered, tertiary-aminoal-20 kyl acrylates and methacrylates, which have repeating units of the following formula:



25 wherein R is an alkylene radical containing at least two carbon atoms, R' is an alkyl radical containing at least three carbon atoms, R'' is an alkyl radical and R''' is selected from the group consisting of H and CH_3 , with R, R', and R''' being selected so that (1) R' and R''' together contain at least five carbon atoms and (2) the sum of the respective steric factors is at least seven. Further description of the steric values for each of R, R' and R''' is given in United States Patent 3,428,711, column 9, lines 18-31. Particularly preferred polymeric tertiary amine stabilizers with which the present invention is particularly useful include poly-(diisopropylaminoethyl methacrylate) and a copolymer of diisopropylaminoethyl methacrylate and decyl methacrylate (sometimes abbreviated "DIPAM/DM"). For the copolymer, the preferred weight ratio of DIPAM to DM monomers is 75 to 25.

30 The titanium dioxide particles that are present in polymer solutions according to the process of the present invention whiten and/or "dull" the filaments spun from the solutions. Rutile TiO_2 is preferred, generally in a concentration in the range of 1 to 7 %, based on the weight of the polymer. A concentration range of 2.5 to 5 % is preferred.

40 It is expected that if the polymeric, sterically hindered, tertiary amines were to be used with acidic inorganic particulate matter other than titanium dioxide, difficulties similar to those described above for the use of TiO_2 and DIPAM/DM additives, would also be encountered with the postulated system. However, it is 45 also expected that addition of an organic base to the postulated system in accordance with the process of the present invention, would also alleviate those difficulties.

50 Note that the organic base must be added to the spandex polymer solution either before the acidic organic particles (e.g., TiO_2) or before the polymeric amine stabilizer (e.g., DIPAM/DM) is added to the solution. Alternatively, the organic base can be added to the solution before both, the TiO_2 and the DIPAM/DM, are added to the solution, provided that the TiO_2 and DIPAM/DM are added separately. These latter two additives must not be permitted to interact before being added to the polymer solution containing the organic base.

55 It is convenient to add the organic base in accordance with the process of the present invention to concentrated solution or slurry of the other additives in the spandex polymer solution. Of course, care must be taken to avoid contact with the TiO_2 additive with the polymeric amine additive before either of these additives are in the presence of the organic base (e.g., diethyl amine). Thus, care must be exercised over the order of addition of ingredients to the polymer solution. A suitable way of accomplishing this requirement is illustrated in the Example below.

Spinning spandex polymer solution containing an organic amine in accordance with the present invention, provides several improvements over spinning the same solutions under the same conditions but without the organic amine. Spinning in accordance with the present invention results in fewer curly filaments, less waste material, longer spinneret life before pluggage, and accordingly, an increase in over-all process yield. Formation of a curly or crimped spandex filament usually accompanies incipient pluggage of a spinneret. The Example which follows demonstrates these advantages.

EXAMPLE

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This example illustrates the dry spinning of spandex polymer solution in a multi-position commercial machine. Each position contains sixteen spinnerets through which a polyether-based spandex polymer solution is dry spun in a conventional manner to form 44-dtex coalesced-filament yarns. Screens are 15 located just upstream of each spinneret. The spun yarns are wound up at conventional speeds.

The dry-spinning procedure used herein was in accordance with the general procedure of Example 1 of Hanzel and Sauer, United States Patent 4,296,174, column 5, line 32-66, the disclosure of which is hereby incorporated by reference. The spandex polymer was formed in N,N-dimethylacetamide (referred to as "DMAC"), solvent, by reacting poly(tetramethyleneether)glycol of 1800 number average molecular weight 20 with p,p'-methylenediphenyl diisocyanate, to form an isocyanate-terminated polyether (also called a "capped glycol"), which was then reacted with an 80/20 molar ratio of ethylene diamine and 1,3-cyclohexylenediamine chain extenders, and with diethylamine for terminating the chain extension. The molar ratio of diamine chain extenders to diethyl amine chain terminator was 6.31 and the ratio of diamine 25 chain extenders to unreacted isocyanate in the capped glycol was 0.948. Substantially all of the amine chain extenders were reacted. The resultant spandex polymer solution contained approximately 36% solids and had a viscosity of about 2100 poises at 40°C. The polymer had an intrinsic viscosity of 0.95, measured at 25°C in N,N-dimethylacetamide at a concentration of 0.5 gram per 100 ml of solution.

In a separate vessel, equipped with a rotating stirrer, the following were mixed in sequence:

- 147.8 kg of dimethyl acetamide,
- 0.51 kg of ultramarine blue pigment (having an average composition of $\text{Na}_5\text{HAl}_4\text{Si}_6\text{S}_4\text{O}_{24}$),
- 31.6 kg of "Santowhite" powder, 1,1-bis (3-t-butyl-6-methyl-4-hydroxy-phenyl) butane antioxidant,
- 49.44 kg of the polymer solution prepared as described in the preceding paragraph,
- 150.0 kg of TiO_2 ,
- 0.695 kg of ethylene diamine,
- 17.6 kg of polydimethylsiloxane silicone oil,
- 0.2 kg of zirconium oxide, and
- 212.6 kg of a copolymer of diisopropylaminoethyl methacrylate and n-decyl methacrylate in a 70/30 weight ratio (DIPAM/DM).

The resultant mixture, which contained 0.15 gram equivalents of amine units per kg of TiO_2 , was then fed to 40 the polymer solution of the preceding paragraph at such a rate that the polymer additives amounted to the following approximate percentages of the final weight of the spandex filaments spun from the polymer solution: 4.5 % TiO_2 ; 6 % DIPAM/DM; 1 % "Santowhite" powder; 0.015 % ultramarine blue; and 0.02 % ethylene diamine.

For comparison, the entire procedure was repeated except that ethylene diamine was omitted from the 45 additives. The comparison procedure duplicated the process and additives used in a conventional commercial process for making of these polyether-based spandex yarns. All weight percentages for these additives were based on the weight of the final filaments.

The advantages of operating according to the present invention, as was done in this Example, over 50 operating in accordance with procedures of the past, as was done in the comparison procedure, is shown by the results summarized in the Table below. The following measures of spinning performance are recorded in the table:

- (a) Spinneret life, the % of spinnerets originally placed into test that still function properly (i.e., do not require replacement) after a given number of hours of spinning;
- (b) Percent of the spinneret changes caused by the formation of curly yarns; and
- 55 (c) Number of broken threadlines per 1,000 kg of 44 dtex yarn produced.

Table

Test	Example	Comparison
% of original spinnerets operating after		
168 hours	28.8	17.2
192 hours	23.4	3.1
216 hours	17.1	0.0
240 hours	11.7	0.0
264 hours	6.3	0.0
288 hours	2.7	0.0
% of spinneret changes due to curly yarns	36.1	76.9
Threadline breaks per ton of yarn produced	12.4	16.7

As can be seen from the preceding table, the procedure of the invention involving the addition of ethylene diamine results in significant advantages over the comparison procedure. Note that, in contrast to the comparison procedure, the procedure of the invention:

- (1) had 67% more of the original spinnerets operating after 7 days of operation (168 hours);
- (2) had 17% of its original spinnerets operating after 9 days (216 hours) versus none for the comparison;
- (3) required fewer than half the number of spinneret changes due to the formation of curly yarns; and
- (4) experienced 26% fewer threadline breaks. As a result, the yield of spandex yarn of satisfactory quality was improved significantly. In addition, the operating life of the screens upstream of the spinnerets was doubled.

Claims

1. In a process for dry spinning spandex filaments wherein a polymeric, hindered tertiary amine stabilizer and acidic inorganic particles are added to a spandex polymer solution prior to spinning, the improvement comprising adding to the polymer solution, either before the addition of the polymeric amine stabilizer or before the addition of the inorganic particles, an effective amount of an organic base.
2. A process of claim 1 wherein the polymeric amine is a sterically hindered, tertiary-aminoalkyl acrylate and methacrylate polymer, the inorganic particles are of titanium dioxide and the organic base is an amine that provides the polymer solution with 0.04 to 1.0 gram equivalent of amine units per kilogram of titanium dioxide.
3. A process of claim 1 wherein the polymeric amine is a sterically hindered, tertiary-aminoalkyl acrylate or methacrylate polymer, the inorganic particles are of titanium dioxide and the organic base is an amine that provides the polymer solution with 0.04 to 1.0 gram equivalents of amine units per kilogram of titanium dioxide.
4. A process of claim 2 or 3 wherein the gram equivalents of amine units per kilogram of titanium dioxide is in the range of 0.1 to 0.5.
5. A process of claim 1 wherein the organic base has a pK_b in the range of 2.5 to 5.0.
6. A process of claim 1, 2, 3, 4 or 5 wherein the organic base is diethyl amine or ethylene diamine.
7. A process of claim 1, 2, 3 or 4 wherein the organic base is diethyl amine or ethylene diamine, the titanium dioxide has a concentration in the range of 1 to 7 percent and the polymeric stabilizer has a concentration in the range of 0.5 to 10 percent, both percentages being based on the weight of the polymer in solution.

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24.05.89 Bulletin 89/21

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DE FR GB IT NL

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(54) Date of deferred publication of the search report:
01.08.90 Bulletin 90/31

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European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 88 31 0786

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	US-A-3 481 905 (HORST WIEDEN et al.) ---		C 08 L 75/04
A	US-A-3 175 990 (EDWARD THEODORE et al.) ---		D 01 F 6/70
D,A	US-A-3 428 711 (OLIVER LARRY HUNT et al.) ---		D 01 F 1/02
A	BE-A- 684 132 (ASAHI KASEI K.K.) -----		
TECHNICAL FIELDS SEARCHED (Int. Cl.4)			
C 08 L C 08 K D 01 F			
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	25-04-1990	BLAS V.M.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
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